Synoptic estimates of diffuse groundwater seepage to a spring-fed karst river at high spatial resolution using an automated radon measurement technique

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Abstract

Groundwater (GW) seepage can provide a major source of water, solutes, and contaminants to rivers, but identifying magnitudes, directions and locations of seepage is complicated by its diffuse and heterogeneous distributions. However, such information is necessary to develop programs and policies for protecting ecosystems and managing water resources. Here, we assess GW seepage to the Ichetucknee River, a spring-fed, low gradient, gaining stream in north-central Florida, through automated longitudinal surveys of radon (^{222}Rn) activities at three different flow conditions. A ^{222}Rn mass balance model, which integrates groundwater and spring water end member ^{222}Rn activities and longitudinal ^{222}Rn distributions in river water, shows that diffuse groundwater seepage represents about 16% of the total river

baseflow, consistent with previous results obtained from ion (Ca^{2+} , Cl^- , SRP and Fe) mass balances and dye tracer methods. During high river stage, the contribution from seepage increases to 18-23% of the river flow. The spatial distribution of GW seepage is more variable in the upper 2.2-km reach of the river than the lower 2.8-km reach, regardless of river flow conditions. The upper reach has a narrower flood plain than the lower reach, which limits evapotranspiration and increases hydraulic gradients toward the river following storm events. Seepage in the lower reach is also limited by hydrologic damming by the receiving river, which inundates the floodplain during high flow conditions, and reduces the hydraulic head gradient. These results demonstrate the variable nature of seepage to a gaining river in both time and space and indicate that multiple synoptic analyses of GW seepage are required to assess seepage rates, determine time-averaged solute fluxes, and develop optimal management policies for riverine ecosystems.

Keywords: Radon, groundwater seepage, groundwater-surface water interaction, karst river, Floridan aquifer,

1. Introduction

Groundwater and surface water are increasingly considered a single system (Sophocleous, 2002; Kalbus et al., 2006), particularly in karst regions where high permeability of conduits and flow paths to sinkholes form a single, dynamic flow system (Katz et al., 1997; Martin and Dean, 2001; Bakalowicz, 2005). Because of hydrologic connection between groundwater and surface water, management of either water resource can alter the quantity and quality of the other. Complete understanding of exchange direction and magnitude between the two sources is therefore required to determine water balances, nutrient dynamics, sustainable limits of groundwater extraction, and to protect the natural flow regime of rivers. Karst aquifers are highly vulnerable and are likely to receive a substantial amount of nutrients and contaminants through agricultural development and land use changes (Coxon, 1999; Katz, 2004). Discharge of nutrient-enriched groundwater into rivers, lakes and estuaries contributes to eutrophication, phytoplankton blooms, and general ecosystem deterioration (Rabalais, 2002; Turner et al., 2003; Katz, 2004). Thus, groundwater discharge to rivers plays a critical role in their hydrological and ecological functions.

The magnitude of groundwater inputs to rivers is controlled primarily by catchment geology, topography and hydrology and often shows high spatial and temporal variability (Woessner, 2000; Sophocleous, 2002; McCallum et al., 2012). These variations can occur along river reaches at scales ranging from cm to km (Woessner, 2000; Storey et al., 2003; Conant, 2004; Poulsen et al., 2015). Groundwater discharge to karst rivers can occur as either discrete flow through conduits (e.g. spring discharge) or diffuse flow through the river bed. Discrete flow to rivers can be directly measured over long reaches using physical techniques such as current meters or by establishing gaging stations; however, quantification of diffuse flow at small scales

remains a challenge because of spatial variability of stream bed properties (Kennedy et al., 2008; McCallum et al., 2012), which is even more challenging for karst aquifers due to their highly heterogeneous nature. Therefore, identifying locations and magnitude of discharge may be useful to evaluate sources of the discharging groundwater, which could be used to assess water quality and quantity.

A number of chemical, physical and numerical techniques have been developed to determine the locations and magnitudes of groundwater discharge into rivers (Kalbus et al., 2006; McCallum et al., 2012; Cook, 2013). Most physically based methods such as seepage meters, head gradients, and temperature gradients provide point measurements that are difficult to extrapolate over larger scales because of the heterogeneous nature of streambed hydrogeological properties (McCallum et al., 2012; Cook, 2013). Application of these point measurements over a large area can be expensive and time consuming, and is limited by the ability to integrate point measurement across the river bed. Other methods such as hydrograph separation and differential flow gaging are associated with high uncertainties that arise from measurement of river flows and estimation of other components of the water balance (Cey et al., 1998; Harte and Kiah, 2009). These methods are only reliable over long river reaches where groundwater input is greater than uncertainty in flow measurements. In contrast, environmental tracers (e.g., stable isotopes, major ions, chlorofluorocarbons, radon) have the potential to provide more accurate and high-resolution information on spatial variability of groundwater inputs at the watershed scale (Cook, 2013). The rate of movement of environmental tracers in a flowing-water system follows physical processes (e.g., advection, dispersion, diffusion, radioactive decay) and the chemical composition of the water evolves over the entire flow path, leaving a distinct chemical signature. These characteristics of environmental tracers provide

advantages over physically based methods and have been used extensively for the past few decades.

One naturally occurring radionuclide of radon (^{222}Rn ; half-life 3.8 days) has proved to be a useful environmental tracer for quantifying groundwater discharge into surface water bodies. ^{222}Rn is an inert gas, generated by the decay of ^{226}Ra within the natural decay chain of ^{238}U to ^{206}Pb . ^{226}Ra is ubiquitous in aquifer materials and its concentration is typically several orders of magnitude higher than dissolved Ra concentration in surface water (Cecil and Green, 2000; Mullinger et al., 2009; Cartwright et al., 2011). ^{222}Rn emitted from these aquifer materials dissolves in groundwater and its short half-life allows ^{222}Rn to reach secular equilibrium with ^{226}Ra in 4 to 5 weeks. When Rn-enriched groundwater discharges into surface water bodies, the ^{222}Rn enrichment decreases because of atmospheric evasion and radioactive decay. Atmospheric evasion and radioactive decay commonly make groundwater ^{222}Rn activities 2-3 orders of magnitude higher than typical surface waters (Burnett et al., 1996, Cable et al., 1996; Corbett et al., 1997). These characteristics have made ^{222}Rn an ideal environmental tracer to identify and quantify groundwater discharge to surface water.

^{222}Rn has been used extensively and successfully to quantify groundwater inflows to rivers (Ellins et al., 1990; Cook et al., 2003, 2006; Mullinger et al., 2007, 2009; Cartwright et al., 2011; Cartwright and Gilfedder, 2015). Despite significant progress using ^{222}Rn tracer to assess groundwater fluxes into rivers, previous studies were based on time-consuming discrete sampling and traditional analysis schemes that limit the ability to make fine-scale assessments of groundwater fluxes over large areas. Burnett et al. (2010) were the first to apply newly developed automated radon detector system to continuously measure ^{222}Rn activity in water along rivers. The basic approach of the automated system is through equilibration of ^{222}Rn in a

constant stream of flowing water with ^{222}Rn in air that is circulated in a closed loop through a ^{222}Rn detector. The activity of ^{222}Rn is determined by collection and measurement of α -emitting polonium daughters, ^{218}Po ($t_{1/2} = 3.1$ min) and ^{214}Po ($t_{1/2} = 164$ μs), which is then estimated as a measure of ^{222}Rn activity in water based on water temperature (Burnett et al., 2001 and Burnett and Dulaiova, 2003). This technique has been used to identify modes (point vs. diffuse discharge) and locations of groundwater discharge reflecting the potential of this technique to be an inexpensive and rapid method to assess groundwater flows into rivers at high spatial resolutions under varying flow conditions.

Most previous studies based on longitudinal river sampling, including Burnett et al. (2010), focused on baseflow condition, without considering temporal variations and hydrological controls on groundwater discharge to rivers. Temporal and spatial variations of exchange could provide information on the nature of discharge (e.g., location and sources), which could be critical for water resource management. Here, we apply an automated radon-in-air technique based on longitudinal measurements of ^{222}Rn activity in the Ichetucknee River in north-central Florida to develop a method that can assess spatial variations of groundwater seepage. Previous work in the region has provided a good understanding of the groundwater inflows to the Ichetucknee River based on ion (Ca^{2+} , Cl^- , SRP and Fe) mass balance and dye tracer methods (Kurz et al., 2015). Thus, this river provides an ideal opportunity to test our automated Rn approach. We also use this method to determine if seepage varies with stream flow conditions, which has not been previously quantified. Our method is based on a mass balance approach of observed ^{222}Rn activities and allows us to quantify diffuse groundwater seepage into the stream over a few tens of meters. Our results indicate that river geomorphology and hydrology can have significant controls on the magnitudes and locations of the diffuse groundwater seepage to rivers.

2. Materials and Methods

2.1. Study Site

The Ichetucknee River is sourced by eight major named springs and numerous small unnamed springs and seeps that discharge from the karstic upper Floridan aquifer (Fig. 1). The river flows about 8 km south-westward from Head Spring before discharging into the Santa Fe River. The Ichetucknee River springshed (the groundwater catchment area that contributes water to the Ichetucknee River) covers an estimated area of 960 km². In the northern part of the springshed, the upper Floridan aquifer, which in this area consists of the Eocene Ocala Limestone, is confined by the clay-rich Miocene Hawthorn Group. The Hawthorn Group has been eroded away in the southern part, leaving the upper Floridan aquifer unconfined. The river is located in the southern portion of the springshed and thus flows directly in contact with the Ocala Limestone, except where sediments armor the bottom of the river (Scott, 1988). Much of the surface runoff in the unconfined area is captured by numerous sinkholes that allow flow directly into the upper Floridan aquifer, which ultimately discharges to the Ichetucknee springs (Butt and Murphy, 2003). Variations in chemical composition of different springs indicate at least two distinct sources of water to the Ichetucknee springs, one representing a shallow and the other a deep flow path (Martin and Gordon, 2000; Martin et al., 2016). Although two sources of water are present, little temporal variation in the composition of the spring waters makes the Ichetucknee River chemostatic (Martin and Gordon, 2000).

The Ichetucknee River has a low gradient (0.7 m/km) and a maximum depth of 3 m during baseflow condition. The river shows distinct geomorphic characteristics between the upper and lower reaches. The major springs are located in the upper reach (Fig. 1c). The portion of the river between Head Spring and Devil's Eye Spring is ~15 m wide, relatively shallow (0.5

– 1 m) and slow-moving (0.15 m/s). The river widens downstream of Devil’s Eye Spring, with widths up to 100 m in an area referred to as the rice marsh (Heffernan et al., 2010). The rice marsh has a narrow main channel that is 1-2 m deep and conducts most of the river flow, whereas the remainder of the channel section on either side is 20-50 cm deep. Downstream of the rice marsh, the channel narrows to approximately 30 m and deepens to 2–3 m, while flow velocities increase to 0.25 m/s. This constrained section has steep channel margins and is surrounded by a wide floodplain (100–300 m on either side) dominated by bald cypress. The Ichetucknee River discharges to the Santa Fe River, which can have elevation changes of 5 m during floods. These floods can hydraulically dam the low-gradient Ichetucknee River, reduce flow velocity and inundate the lower-reach floodplain.

The Ichetucknee River at the US27 Bridge has an average discharge of 8.5 m³/s and has ranged from 3.5 to 19.9 m³/s (2002–2014, U.S. Geological Survey, 2015). The river receives most of its flow from the six largest springs (Head, Cedar, Blue Hole, Mission, Devil’s Eye and Mill Pond, Fig. 1c). Like other springs that originate from the upper Floridan aquifer, the springs in the Ichetucknee River show stable discharge throughout the year, with generally muted response to rainfall events (Martin and Gordon, 2000; Florea and Vacher, 2006). Continuous measurements of hydraulic head gradients at multiple locations in the river indicate persistent gaining conditions (Kurz et al., 2015), consistent with the regional potentiometric surface map of the upper Floridan aquifer (Fig. 1b; Sepulveda et al., 2006).

2.2. Field Survey, Water Sampling and Radon (²²²Rn) Measurement

Field measurements of the longitudinal distribution of ²²²Rn in the river water were carried out on three occasions that correspond with baseflow (8 Feb 2013), rising river stage (23 Apr 2014) and falling river stage (23 May 2014) (Fig. 2). The techniques employed for ²²²Rn

survey were based on Dulaiova et al. (2005) and Burnett et al. (2010). Briefly, three radon-in-air monitors (RAD7, DurrIDGE Co.) were connected in parallel to an air-water equilibrium spray chamber via a closed air loop. River water from 50 cm depth was pumped into the equilibrium chamber at the rate of approximately 5 L/min where the ^{222}Rn within the air loop equilibrated with the ^{222}Rn in the water. RAD7s were run in sniff mode which determines the activity of ^{222}Rn in air by counting its short-lived α -emitting daughter ^{218}Po . The activity of ^{222}Rn in water was calculated from the temperature-dependent distribution factor, k_l , of radon activity between water and air, which can be calculated by:

$$k_l = 0.105 + 0.405 e^{-0.0502T} \quad (1)$$

(Weigel, 1978) where T is temperature of water in °C. Because of high ^{222}Rn activity in river water, we were able to achieve radon measurements with precision of about 15% (1σ) at two minutes integration time. The automated system was used in conjunction with a GPS to log locations and YSI Pro Plus to log hydrological variables, including temperature and specific conductance at one-minute time interval. The system was deployed in a small metal boat, which was paddled slowly (2-3 km/hr) around 5 km downstream from the Head Spring to the southern take-out point just upstream from the US27 Bridge, yielding ^{222}Rn measurements at intervals of 60 to 100 m. Because we estimated response time of ^{222}Rn in our RAD7 setup to be around 20 minutes, we matched the ^{222}Rn measurement points to the instrument sampling location 20 minutes prior to determine the exact locations of measured ^{222}Rn in the river water.

Discrete water samples were collected in pre-evacuated 1-liter glass bottles from end member sources including the major springs, river, piezometers installed into river bed sediments, and small spring seeps five times on Dec 2012, March 2013, Nov 2013, Feb 2014 and Aug 2014 (Fig. 1c) to determine their ^{222}Rn and ^{226}Ra activities, the parent isotope of ^{222}Rn . Prior

to sampling, hydrological variables (temperature and specific conductance) were measured using the YSI Pro Plus. The water samples for ^{222}Rn were analyzed using a modified Big Bottle RAD H_2O technique (Lee and Kim, 2006). This technique employs a closed loop aeration scheme, in which a sample bottle is connected to a radon-in-air monitor (RAD7, DurrIDGE Co.) and ^{222}Rn is extracted from the water by continuous recirculation of air through the water until the water equilibrates with the air. The ^{222}Rn activity in a water sample at the time of measurement (C_w , Bq/m^3) is calculated based on the activity of radon in air, air volume and water volume, according to

$$C_w = \frac{Ca*(Va+k_1*Vw)-Cb*Va}{Vw} \quad (2)$$

(Lee and Kim, 2006) where Ca is the equilibrium ^{222}Rn activity in air (Bq/m^3), Va is total volume of air in the system (L), k_1 is the distribution ratio calculated using equation (1), Vw is volume of water in sample bottle (L), and Cb is the background ^{222}Rn activity in air (Bq/m^3). ^{222}Rn activities calculated using equation (2) were decay-corrected back to the time the samples were collected. All samples were analyzed within 24 hrs of collection. After the initial ^{222}Rn analysis, the samples were sealed and stored for a month to allow ^{222}Rn to come into secular equilibrium with ^{226}Ra . After one month, the samplers were re-measured for ^{222}Rn activity, using procedures identical to those used to measure the dissolved ^{222}Rn activity at the time of collection. This ^{222}Rn activity was assumed to represent the activity of ^{226}Ra in water.

Sediment-supported ^{222}Rn activities were determined using the sediment equilibration technique (Martens et al., 1980). Approximately 50 gm of river bed sediment was weighed and mixed with 300 ml river water of known ^{226}Ra activity in a 500 ml flask. The water was analyzed for ^{222}Rn activity by RAD H_2O techniques as described above after a 30-day in-growth period assuming ^{222}Rn in water reached equilibrium with the fraction of ^{226}Ra in sediments that would

yield ^{222}Rn to the water. The activity per mass of sediment was converted to an equivalent activity per volume of pore water using measured sediment porosity and wet bulk density.

2.3. Radon (^{222}Rn) Mass Balance Model

Estimates of groundwater discharge to the river are based on a mass balance box model that accounts for all radon sinks and sources to the river (Fig. 3). The study reach was divided into discrete boxes (60 to 100 m long), each enclosed by upstream and downstream ^{222}Rn measurements from the RAD7. Because the Ichetucknee River receives no water from overland flow or tributaries, the steady-state water mass balance in each box per unit time interval can be described as:

$$Q_o = Q_i + Q_{gw} + Q_{sp} - E \quad (3)$$

where Q_o is river flow at the downstream section (m^3/s), Q_i is river flow at the upstream section (m^3/s), Q_{gw} is diffuse groundwater discharge (m^3/s), Q_{sp} is spring input (m^3/s) and E is evaporation normalized to water surface area (m^3/s). Based on these flows, we can use a ^{222}Rn mass balance to determine the average groundwater discharge that would be expected in each box. To evaluate the groundwater contribution to the Ichetucknee River, all possible sources and sinks of ^{222}Rn must be considered. ^{222}Rn activities in a river are primarily governed by river water-groundwater exchange through both advection and diffusion, radioactive decay, atmospheric evasion, production in the water column and evaporation (Fig. 3). Assuming steady-state conditions and a well-mixed water column, the radon mass balance within a portion of the river length can be expressed as:

$$Q_o Rn_o + F_{atm} + F_{dec} + F_{evp} + F_{dif} = Q_{gw} Rn_{gw} + Q_i Rn_i + Q_{sp} Rn_{sp} + F_{pro} + F_h \quad (4)$$

where Rn_o , Rn_{gw} , Rn_i , and Rn_{sp} are the ^{222}Rn activity in the downstream river section, groundwater, upstream river section, and spring water, respectively. All Rn activities are

reported in Bq/m³. All F terms are ²²²Rn fluxes not associated with water flows and are expressed as activity per unit time (Bq/s), taking into account the surface area or volume of each box. F_{atm} is the ²²²Rn flux to the atmosphere, F_{dec} is radon decay in the water column, F_{evp} is the ²²²Rn loss to evaporation, F_{dif} is the ²²²Rn diffusion flux from water column to river bed sediments, F_{pro} is radon production in the water column from ²²⁶Ra and F_h is radon flux from hyporheic zone. All the terms on the left side of Eq. 4 represent ²²²Rn sinks and on the right side represent ²²²Rn sources. Considering a discrete approach at steady state, Eq. 4 can be simplified to estimate the diffuse groundwater discharge to the river:

$$Q_{gw} = (Q_o Rn_o + F_{atm} + F_{dec} + F_{evp} + F_{dif} - Q_i Rn_i - Q_{sp} Rn_{sp} - F_{pro} - F_h) / Rn_{gw} \quad (5)$$

The losses of ²²²Rn resulting from atmospheric evasion and decay (F_{atm} and F_{dec} , respectively) are functions of average ²²²Rn activity in the water column within a reach (Rn_r).

$$F_{atm} = k_2 A Rn_r \quad (6)$$

$$F_{dec} = \lambda V Rn_r \quad (7)$$

where k_2 is the gas transfer velocity (m/s), A is the surface area of the reach (m²), V is the volume of the reach (m³) and λ is the decay constant of ²²²Rn ($2.11 \times 10^{-6} \text{ s}^{-1}$). The gas transfer velocity (k_2) is a key variable and probably the biggest source of error in using radon for estimating groundwater discharge. Several different approaches exist to estimate k_2 , including the use of empirical formulae relating k_2 as a function of physical characteristics of rivers (e.g. O'Conner and Dobbins, 1958; Hammond and Fuller, 1979; Mullinger et al., 2007), direct measurement using introduced gas tracers such as propane or SF₆ (e.g. Genereux and Hemond, 1992; Wallin et al., 2011) and estimate from modelling exercises by matching the predicted and observed data (e.g. Cook et al., 2003; Cartwright et al., 2014). Gas tracers are usually used along small rivers or along small reaches of a river that may not be representative of the river as a whole. Data fitting

approaches are suitable only in losing reaches or reaches where groundwater inflows are known. Because of their limitations, gas tracers and data fitting approaches may not be applied in a large and gaining river like Ichetucknee. Because flow-generated turbulence is important in controlling gas transfer velocity in streams and rivers, we used an equation proposed by O'Conner and Dobbins (1958) and Hammond and Fuller (1979) to estimate k_2 as:

$$k_2 = (D_m v/h)^{1/2} \quad (8)$$

where D_m is molecular diffusion coefficient corrected for water temperature ($-\log D_m = 980/T + 1.59$; Peng et al., 1974), v is average current velocity (m/s), and h is water column height (m).

The diffusive flux (F_{dif}) across sediment-water interface was calculated using a Martens et al. (1980) depth-independent equation:

$$F_{dif} = (D_s \lambda)^{1/2} (Rn_{eq} - Rn_r) \quad (9)$$

where Rn_{eq} is radon concentrations in equilibrium with sediment ^{226}Ra and Rn_r is radon concentrations at the sediment-water interface, and is assumed to be equal to the value for the water column. D_s is the sediment diffusion coefficient, which was estimated for measured average porosity (ϕ) of 0.56 after correcting for sediment tortuosity ($D_s = \phi^2 D_m$; Ullman and Aller, 1982). The sediment diffusion coefficients for all sampling sites and times ranged from 3.9×10^{-10} to $6.7 \times 10^{-10} \text{ m}^2/\text{sec}$ with an average value of $4.9 \times 10^{-10} \text{ m}^2/\text{sec}$.

Radon production in the water column from ^{226}Ra (F_{pro}) was calculated as:

$$F_{pro} = \lambda_{Ra} V R a_r \quad (10)$$

where λ_{Ra} is the decay constant of ^{226}Ra ($1.4 \times 10^{-11} \text{ s}^{-1}$) and $R a_r$ is activity of radium (^{226}Ra) in the Ichetucknee River water column, which ranges from 13 to 26 Bq/m³ with an average value of $18 \pm 1.6 \text{ Bq/m}^3$. All parameters used in the mass balance calculations are listed in Table 1.

3. Results

3.1. Hydrologic Variations

Discharge data from each of the six main springs (Head, Cedar, Blue Hole, Mission, Devil's Eye and Mill Pond), from which the river receives most of its flow, and the river at US27 Bridge were obtained from the USGS through June 2010, when all gages except at Blue Hole (the largest spring) and the US27 Bridge were discontinued. Regressions between archived flow at each spring (prior to June 2010) and flows at Blue Hole and US27 Bridge were used to reconstruct daily spring discharge during the study period. Two other third-magnitude springs (Grassy Hole and Coffee) contribute less than 1% to the river discharge.

During the study period (Feb 2013 to May 2014), the discharge of the Ichetucknee River at the US27 Bridge ranged from 3.9 to 13.9 m³/s, with an average discharge of 9.39 m³/s (Fig. 2). River discharge during baseflow conditions correlates positively with river stage. In contrast, following a high rainfall event in April 2014, river stage at the US27 Bridge increased rapidly from 4.6 m to 7.8 m, while the associated river discharge dropped from 9.8 to 3.9 m³/s (Fig. 2) as a result of hydraulic damming. As the river stage receded following the rainfall event, the river discharge increased to a value greater than pre-rainfall discharge, reaching a peak discharge of 11.8 m³/s, in 10 days. Similar responses were observed in Blue Hole Spring discharge and stage to the high rainfall event (Fig. 2). Stage rose by 1 m and, consequently, spring discharge dropped by 1.4 m³/s. Following the water level recession, spring discharge quickly rose and stayed above the pre-event value for several months. Mean daily river flow recorded at the US27 Bridge on the survey days, 8 February 2013, 23 April 2014 and 23 May 2014, were 8.7, 7.4, and 8.9 m³/s, respectively.

3.2. River Longitudinal Surveys

The river flow changed little during the surveys considering the coefficient of variations (ratio of standard deviation to mean) of hourly measurements of flow at the US27 Bridge were 0.4, 3.6 and 3.9% on 8 February 2013, 23 April 2014 and 23 May 2014, respectively. The three surveys showed significant spatial and temporal variations in longitudinal distribution of ^{222}Rn activities (Fig. 4a). ^{222}Rn activities ranged from 9000 to 13,741 Bq/m³ along the river on 8 February 2013 during baseflow condition, whereas the activities were lower and ranged from 3299 to 7645 Bq/m³ and 6142 to 10,686 Bq/m³ on 23 April 2014 during rising river stage and 23 May 2014 during falling stage, respectively. Variation of ^{222}Rn activities during baseflow and falling river stage showed similar pattern with decreasing concentration gradients from upstream to downstream. The upper reach displayed smaller downstream gradients of ^{222}Rn activities than the lower reach reflecting the presence of all but one named spring (Coffee Spring), which provide most of the ^{222}Rn to the river. The survey on 23 April 2014 during rising river stage showed the opposite trend with activities of ^{222}Rn consistently increasing downstream.

Specific conductance (SpC) and temperature varied along the river and between surveys (Fig. 4b and 4c). Both parameters had greater variability in the upper than lower reach. Relative to river hydrology, both parameters had the greatest values during the falling river stage on 23 May 2014 and lowest values during the baseflow condition on 8 February 2013. The SpC values of the river water remained constant at the headwater until 350 m downstream, at the confluence with Blue Hole spring run where they dropped by 17 to 34 $\mu\text{S}/\text{cm}$, depending on stage and then rose gradually downstream regardless of the river hydrologic conditions. Average conductivities in grab samples from groundwater (piezometer water and small spring seeps), spring water, and river water over the survey period were 328 ± 12 , 341 ± 9 , and 325 ± 32 $\mu\text{S}/\text{cm}$, respectively and

were not statistically different ($p > 0.05$) preventing their use in separating these sources of water to the river.

During baseflow, water temperature varied little (from 21.5 to 21.7 °C) with slightly higher temperature in the upper reach than the lower reach. During both rising and falling river stage, temperature increased in the upper reach to approximately 2000 m downstream, dropped until river distance 4500 m and then rose to the end of the transect. These temperature variations ranged from 21.3 to 22.5 °C and 21.8 to 23 °C, respectively. Average groundwater temperature was 21.9 ± 0.5 °C. Small difference in temperature between groundwater and river water also limits its use to separate water sources.

3.3. End-member ^{222}Rn activities

Each spring displayed a unique ^{222}Rn activity that ranged from 9842 at Mill Pond Spring to 21,608 Bq/m³ at Devil's Eye Spring. Individual springs showed no significant temporal variations ($p > 0.05$) in ^{222}Rn activities. The average ^{222}Rn activity in all springs at all times is estimated to be $16,150 \pm 1330$ Bq/m³, which is around twice the value of the river water (Fig. 5). Pore water from the piezometers yielded ^{222}Rn activities between 3922 and 6225 Bq/m³, with an average value of 4512 ± 290 Bq/m³. Water seeping through small unnamed springs had ^{222}Rn activities that ranged between 5083 and 7029 Bq/m³ with average value of 5930 ± 420 Bq/m³, slightly higher than the pore water and around three times smaller than the spring values. Because of the similar and relatively low ^{222}Rn activities in pore water and small spring seep samples, the average ^{222}Rn activity (5285 ± 370 Bq/m³) was used as the end-member value for groundwater seepage in the mass balance model. Hereafter, pore water from the piezometers and seeps through the small springs are collectively regarded as representative of diffuse groundwater. Head Spring was regarded as the headwater and the rest of springs were treated as

tributaries for the mass balance model. The lack of significant temporal variations in spring water and groundwater end members allowed us to use average values over the sampling time in the mass balances for all survey periods.

4. Discussion

4.1. Radon (^{222}Rn) Distributions, Sources and Sinks

Groundwater typically has radon activities that are 2-3 orders of magnitude higher than surface water, due to ^{222}Rn sources in the groundwater from radioactive decay of sedimentary ^{226}Ra and loss from surface water from radioactive decay and evasion to the atmosphere (Cable et al. 1996; Burnett and Dulaiova, 2003). The elevated ^{222}Rn activity in the Ichetucknee River relative to groundwater (Fig. 5) is in contrast to this more common situation because of rapid discharge of high ^{222}Rn activity water from the head springs. Elevated ^{222}Rn activity in spring water could originate from at least three sources: (1) uranium-bearing phosphate minerals in Hawthorn Group sediments (Scott, 1988), (2) ^{226}Ra co-precipitated in Fe-Mn oxides within the Floridan aquifer on conduit walls (Brown et al., 2014; Gainon et al., 2007; Eross et al., 2012), and (3) uranium in the carbonate mineral of the Floridan aquifer. In contrast, the diffuse groundwater seeping to the river would discharge from porous matrix of the aquifer which would limit oxygen contents and Fe-Mn oxide phases. Flow through the matrix porosity is slower than in conduits (Martin and Dean, 2001), allowing ^{222}Rn to decay before seeping to the river. Regardless, determining sources of ^{222}Rn is unnecessary to this study because samples of end-member allows systematic separation of sources downstream along the study reach.

Contributions from these spring sources are superimposed on the overall downstream loss from evasion. Gas transfer velocities are 1.1 ± 0.3 , 0.6 ± 0.2 and 0.7 ± 0.2 m/day during baseflow (8 Feb 2013), rising river stage (23 Apr 2014) and falling river stage (23 May 2014), respectively.

Low gas transfer velocities in the Ichetucknee River are a consequence of the low channel gradient and resulting slow velocity and are consistent with values in low-gradient rivers elsewhere, which range from 0.5 to 2.5 m/day (e.g., Raymond and Cole, 2001; Cook et al., 2003; Cartwright et al., 2011). Significant evasion must occur at or near the spring boils prior to flowing into the main river channel, resulting in the lower ^{222}Rn activities of the river compared with the springs.

Although multiple processes are included in the mass balance model (Eq. 5), only a few constitute major sources and sinks and some are sufficiently small that they can be neglected. Atmospheric evasion, governed by gas transfer velocity, is the major ^{222}Rn sink in the mass balance model and causes 80%, 56% and 61% of ^{222}Rn loss during baseflow, river rising stage and river falling stage, respectively (Table 2). More ^{222}Rn degasses during high than low stage because of reduced flow velocity following hydrological damming of the river. Radioactive decay represents 20%, 44% and 39% of the sink during baseflow, river rising stage and river falling stage, respectively. Diffusion is a sink of ^{222}Rn in the Ichetucknee River because the Ichetucknee River surface water has higher ^{222}Rn activity than the pore water in the bed sediments. We measured ^{222}Rn diffusive fluxes only once during baseflow condition, which ranged from 4.9 to 6.8 $\text{Bq m}^{-2} \text{ day}^{-1}$ with an average value of 5.5 $\text{Bq m}^{-2} \text{ day}^{-1}$ (Table 2). We applied this value to all flow conditions although the loss could change as river water ^{222}Rn activities change (e.g., Fig. 4a). However, ^{222}Rn loss due to diffusion is <1% of the total loss suggesting its variability with changes in river conditions is negligible. Estimates of evaporation, made from potential evaporation data (Florida Automated Weather Network, 2015) and the river water surface area during the survey period, account for only 0.07% of daily river flow, indicating a negligible amount of ^{222}Rn loss from the river attributable to evaporation.

Radon produced by ^{226}Ra in the water column is the only ^{222}Rn source not associated with water flow. The estimated value averages $4.9 \times 10^{-5} \text{ Bq m}^{-2} \text{ day}^{-1}$, or about ten orders of magnitude smaller than the ^{222}Rn activities and therefore can be ignored in the model. The hyporheic zone could also contribute ^{222}Rn to river water and its exclusion from mass balance modeling could overestimate groundwater seepage up to 70% (Cook et al., 2006; Cartwright et al., 2011). However, no hyporheic exchange was found in the Ichetucknee River based on a dye tracer study due to low hydraulic conductivity of river-bed sediments (Hensley and Cohen, 2012). In addition, errors associated with hyporheic exchange, if there is any, would be non-significant in mass balance calculation because the Ichetucknee River and groundwater have usually high ^{222}Rn activities. The only other sources of ^{222}Rn in addition to those shown in Table 2 include diffuse groundwater seepage and spring discharge.

4.2. Evaluation of the Automated ^{222}Rn Technique

Our radon mass balance shows that Ichetucknee River gains water along the entire study reach (Fig 6). Kurz et al. (2015) obtained similar estimates of gaining water for the Ichetucknee River at baseflow using two independent methods, an ion (Ca^{2+} , Cl^- , SRP and Fe) mass balance and based on an injected dye trace. Although not conducted simultaneously, Kurz et al. (2015) study provides a reasonable comparison to our work because springs and river discharge in the Ichetucknee River system are stable during baseflow. To compare with the Kurz et al. (2015) results, we estimated the cumulative diffuse groundwater seepage to the river by summing the values under the curve representing baseflow (8 Feb 2013) shown in figure 6. These estimates indicate the river gained around $1.2 \times 10^5 \text{ m}^3/\text{day}$, or about 16% of the total river flow at that time (Fig. 7). This result is consistent with gains estimated from both the dye tracer and ion mass balance methods, which are $1.1 \times 10^5 \text{ m}^3/\text{day}$ and $0.9 - 1.3 \times 10^5 \text{ m}^3/\text{day}$, respectively (Kurz et

al., 2015). Consistency of results from these three methods gives confidence in the automated ^{222}Rn technique for synoptic assessments of groundwater seepage into streams and rivers.

No independent results are available to compare with our results during high river stage conditions (23 April 2014 and 23 May 2014). Assuming the ^{222}Rn model can be applied during non-baseflow conditions, our technique estimates around 15-42% more water gained during high river stage than base flow. These gains account for 18-23% of the total river flow (Fig. 7). The estimated diffuse groundwater seepage to the river likely represents a mixture of vertical flows through the river-bed sediments and seeps through the small, unnamed springs that originate from the upper Floridan aquifer (Kurz et al., 2015). Because these two sources have similar ^{222}Rn activities, the Rn mass balance model cannot be used to separate the contribution of each source. However, a previous estimate based on phosphorous mass balance (Kurz et al., 2015) showed that groundwater seepage through river-bed sediments and through small springs represent 23% and 77% of total diffuse groundwater seepage, respectively. Because groundwater seeping through river-bed sediments could be a source of recycled solutes and the groundwater seeping through small springs could be source of new solutes, the relative contribution of these two groundwater pathways may be critical for understanding river biogeochemical cycles.

High degrees of uncertainty in the calculations of groundwater seepage using the ^{222}Rn mass balance method result from high spatial and temporal variability of ^{222}Rn activity in the groundwater end member, difficulty in accurate determination of gas transfer velocity and poorly constrained hyporheic exchange (Cook, 2013; Cartwright and Gilfedder, 2015). As discussed above, error associated with hyporheic exchange, which is minimal at this site, can be ignored. We used standard error as a measure of variability in groundwater ^{222}Rn activities and gas transfer velocity to determine the uncertainties associated with these terms. The standard error of

groundwater ^{222}Rn activity is 370 Bq/m^3 , which produces an uncertainty of about $\pm 12\%$ in the cumulative groundwater seepage into the river. The standard errors of gas transfer velocities during baseflow, rising river stage and falling river stage are 0.3, 0.2 and 0.2 m/day, respectively which result an uncertainty of $\pm 4\text{--}10\%$ in cumulative groundwater seepage with the highest uncertainty occurring at baseflow. Because techniques and methods developed for estimating groundwater seepage operate over a range of spatial and temporal scales and each is associated with limitations and uncertainties, a multi-scale approach combining multiple techniques are preferable for more accurate and better characterization of groundwater-surface water interactions than single method (Sophocleous, 2002; Kalbus et al., 2006; Cook, 2013). However, low degree of uncertainties and consistent results with previous study provides some confidence in automated ^{222}Rn measurement technique for synoptic assessment of groundwater seepage into the rivers.

4.3. Geomorphological and Hydrological Controls on Groundwater Seepage

The upper reach of the river, with the greatest seepage of low ^{222}Rn activity water (Fig. 6), coincides with the highest ^{222}Rn activities in the river water (Fig. 4a). These elevated ^{222}Rn activities result from discharge from the majority of the major source springs, which keep the river water ^{222}Rn activities high despite the diffuse groundwater seepage with low ^{222}Rn . Thus, the spatial distribution of ^{222}Rn activity in river water does not directly reflect spatial patterns of groundwater inflows. Furthermore, river flow conditions are important, with the greatest gains occurring during the river rising stage (average $33 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$), followed by river falling stage (average $26 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$), with the lowest gains during baseflow condition (average $22 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$; Fig. 6).

Although river flow conditions affect the magnitude of groundwater seepage to the river, the spatial patterns of seepage are similar regardless of flow and coincide with changes in the river and flood plain morphology. The upper reach, which is characterized by the greatest gains (Fig. 6), has a narrower flood plain with a steeper slope toward the river than the lower reach (Fig. 1c). This morphology should create a steeper hydraulic gradient than in the lower reach. Hydraulic head gradients from the flood plain to the river measured at the rice marsh in the upper reach from December 2009 through October 2012 were consistently higher than in the lower reach at Dampier's Landing regardless of seasons (Kurz et al., 2015). The wide valley in the lower reach results in flood plains extending up to 300 m on either side of the river, which may enhance evapotranspiration and result in a lower groundwater table and hydrologic gradient there (e.g., Doble et al., 2006; Schilling et al., 2006). Greater evapotranspiration in the lower than upper reaches is supported by long-term SpC data, collected using CTDs at 15 minutes interval from Dec 2009 through Oct 2012, of pore water that is 443 $\mu\text{S}/\text{cm}$ at Dampier's Landing compared with 362 $\mu\text{S}/\text{cm}$ at the rice marsh. River geomorphology, particularly flood plain width, thus appears to be a controlling factor in the spatial distribution of groundwater seepage to the river, as indicated by their negative correlation (Fig. 8). However, the occurrence of the lowest fluxes of groundwater in the uppermost river reach, in the first 500 m downstream of Head Spring (Fig. 6), and their non-correlation with flood plain width suggest that regional hydrogeology and groundwater flow paths could also influence groundwater seepage besides the river geomorphology. The spring group near the headwaters (Head, Cedar and Blue Hole) is sourced from a shallow young groundwater component, while the downstream spring group (Mission, Devil's Eye and Mill Pond) is sourced by a deep old groundwater (Martin and Gordon, 2000; Martin et al., 2016). A shallow conduit networks could drain the aquifer up-gradient from

the head springs, which would reduce groundwater seepage. Draining through conduits is supported by the flat potentiometric surface northeast of the head spring region (Fig. 1b). Downstream of this region, deep flow paths would not affect the shallow groundwater hydraulic gradients and increase the groundwater seepage to the river compared with the headwaters (Fig. 6).

The spatial differences in diffuse groundwater seepage from the upper to lower reach are amplified during rising river stage on 23 April 2014 (Fig. 6). The recharge rate in the unconfined upper Floridan aquifer is high, with a range of 40-80 cm per year (Grubbs, 1998) and thus rainfall, in addition to being correlated to river flow conditions, would also directly recharge the shallow aquifer and increase the head gradient toward the river. During the regression from the elevated stage, the head gradients would relax, reducing seepage to the river gains during the recession, ultimately returning to the background seepage occurring during baseflow. In contrast, gains to the lower river reaches vary less with river flow than the upper reach (Fig. 6). The difference in gains indicates a similar increase in head gradient, and linked groundwater input to the river, does not occur in the lower reach. Decreases in head gradients could result from hydrologic damming with elevated Santa Fe River stage. In addition, enhanced evapotranspiration would limit the recharge in this region also reducing the amount of discharge to the river.

Groundwater seepage to streams and rivers provides essential solutes (nutrients and carbon) to river water and thus composition, dynamics and richness of riparian and sub-aquatic vegetation are associated with high seepage zones (Roy et al., 2011; Kuglerova et al. 2014). These seepage zones can be important thermal refugia for various aquatic animals as well (Loheide and Gorelick, 2006). Groundwater usually has low dissolved oxygen and is chemically

reducing and thus, the seepage zones may affect fish spawning by inhibiting embryo development (Malcolm et al., 2005). Most work linking ecosystem function with groundwater seepage typically considers only spatially variability, but results presented here demonstrate that groundwater seepage also varies with river flow condition, a characteristic that should be considered in linking groundwater seepage to ecosystems. Specific to Ichetucknee River, seepage rates are greatest after large rainfall-events and lowest at baseflow. Seepage transport of nutrients (P, N) and carbon are thus also linked to discharge conditions (Kronvang and Bruhn, 1996; Stutter et al., 2008; Khadka et al., 2014). Understanding temporal variations requires the ability for rapid and synoptic measurements of seepage rates and locations, such as provided by the ^{222}Rn technique described here.

5. Conclusion

Three synoptic, continuous and automated longitudinal ^{222}Rn surveys allowed estimates of diffuse groundwater seepage to the Ichetucknee River at high spatial resolution during different river flow conditions. Seepage estimates during baseflow are consistent with previously measured baseflow groundwater discharge based on dye tracer and ion mass balance methods, which suggests that the automated ^{222}Rn technique is useful for rapid, inexpensive and synoptic assessments of groundwater discharge into streams and rivers. The technique is applicable in all stream and river systems where groundwater and surface water possess distinct ^{222}Rn activities. The potential for measurements of changes in gains to rivers provides an important method to understand the relationship between discharge conditions, river morphology characteristics, and river inputs. Specifically, our results indicate that the location and magnitude of diffuse groundwater seepage to Ichetucknee River are controlled by river hydrology and morphology, particularly the width of the flood plain and hydrologic damming of the receiving stream. This

high spatial resolution and synoptic method can thus provide an improved understanding of groundwater discharge to rivers, which is a critical factor for water resources management and for river ecosystem assessment.

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Figure Captions

Fig. 1. Location map of the study site. a) Regional location map showing the distribution of confined, semi-confined, and unconfined Floridan aquifer. b) Regional potentiometric surface map of the upper Floridan aquifer in the Ichetucknee region (Sepulveda et al., 2006). c) Lidar image of Ichetucknee River and springs with sample locations and delineation of flood plain (black line).

Fig. 2. Hydrologic variation in the Ichetucknee River recorded at US27 Bridge and Blue Hole Spring during the study period. The low discharge during times of high river stage in May 2014 reflects hydrologic damming by the Santa Fe River. Times of ^{222}Rn surveys are indicated by black arrows.

Fig. 3. A schematic diagram showing the various sources and sinks of ^{222}Rn in a river system. All relevant symbols are defined in text.

Fig. 4. Distribution of a) ^{222}Rn , b) specific conductance and c) temperature along the Ichetucknee River during baseflow, rising river stage and falling river stage. Arrows on the top indicate spring inflows into the river; HS-Head, CE-Cedar Spring, BH-Blue Hole, MS-Mission, DE-Devil's Eye, GS-Grassy, MP-Mill Pond and CS-Coffee Spring. The vertical dashed line represents the location of the change in channel configuration between the upper and lower reaches.

Fig. 5. Box and whisker plot showing distribution of ^{222}Rn activities in spring water, river water, seep water from small springs, and pore water from piezometer installed into river bed sediments. River water data are from grab samples in upper section of the river.

Fig. 6. Spatial and temporal variations of groundwater inflows into the Ichetucknee River, calculated from the ^{222}Rn mass balance model. Arrows on the top indicate spring inflows into the river; HS-Head, CE-Cedar Spring, BH-Blue Hole, MS-Mission, DE-Devil's Eye, GS-Grassy, MP-Mill Pond and CS-Coffee Spring. The vertical dashed line represents the location of the change in channel configuration between the upper and lower reaches.

Fig. 7. Cumulative groundwater discharge to the Ichetucknee River during three different flow stages. Data for ion mass balance and dye tracer are from Kurz et al. (2015).

Fig. 8. Spatial distribution of measured diffuse groundwater seepage relative to river flood plain width. Data points enclosed by oval are from the upper most river reach to around 500 m downstream of Head Spring and are controlled by groundwater flow paths rather than flood plain width. Trend lines excludes those data.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1. Summary of the parameters used in mass balance model

Parameter	Symbol	Unit	Values	
			Baseflow (2-8-2013)	Rising stage (4-23-2014)
Intitial upstream flow	Q_i	m^3/s	1.76	1.74
Intitial upstream ^{222}Rn activity	Rn_i	Bq/m^3	13172	3299
^{222}Rn activity along the river	Rn_r	Bq/m^3	9000 - 13741	3299 - 7645
Spring discharge	Q_{sp}	m^3/s	0.25 - 2.72	0.25 - 2.69
Spring water ^{222}Rn activity	Rn_{sp}	Bq/m^3	9842 - 21608	9842 - 21608
GW Rn activity	Rn_{gw}	Bq/m^3	5285	5285
River width	w	m	15 - 75	15 - 75
River depth	h	m	1 - 2.5	1.5 - 4.5
Evaporation	E	m/day	3.7×10^{-3}	3.7×10^{-3}
River velocity	v	m/s	0.2	0.1
Gas transfer velocity	k_2	m/day	1.1	0.6
Decay constant of ^{222}Rn	λ	s^{-1}	2.09×10^{-6}	2.09×10^{-6}
Decay constant of ^{226}Ra	λ_{Ra}	s^{-1}	1.4×10^{-11}	1.4×10^{-11}
River water ^{226}Ra activity	Ra_r	Bq/m^3	18	18
Molecular diffusion coefficient of ^{222}Rn	D_m	m^2/s	1.23×10^{-9}	1.23×10^{-9}
Sediment diffusion coefficient of ^{222}Rn	D_s	m^2/s	4.9×10^{-10}	4.9×10^{-10}
^{222}Rn in equilibrium with river sediment	Rn_{eq}	Bq/m^3	7600	7600

Table 2. The activity loss or gain of ^{222}Rn (not associated with water flow) in the Ichetuck terms are expressed in $\text{Bq m}^{-2} \text{ day}^{-1}$. Positive (+) and negative (-) symbols represent source the river water column, respectively.

Parameters	Symbol	Baseflow (8 Feb 2013)	Rising Stage (23 Apr 2014)
Atmospheric evasion (-)	F_{atm}	12848 ± 181	3549 ± 66
Radioactive decay (-)	F_{dec}	3170 ± 45	2826 ± 53
Diffusion (-)	F_{dif}	5.5 ± 0.4	
Water column production (+)	F_{pro}	$3.3 \times 10^{-5} \pm 2.9 \times 10^{-6}$	$5.7 \times 10^{-5} \pm 5.1 \times 10^{-6}$